Use of poly(3-hexylthiophene)/poly(methyl methacrylate) (P3HT/PMMA) blends to improve the performance of water-gated organic field-effect transistors

Loig Kergoat, Nicolas Battaglini, Luciano Miozzo, Benoit Piro, Minh-Chau Pham, Abderrahim Yassar, Gilles Horowitz

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Corresponding Author: PROF GILLES Horowitz,

Corresponding Author's Institution: University Paris Diderot

First Author: Gilles Horowitz

Order of Authors: Gilles Horowitz; Loïg Kergoat; Nicolas Battaglini; Luciano Miozzo; Benoit Piro; Minh-Chau Pham; Abderrahim Yassar

Cover Letter

This is the cover letter for the paper entitled "Use of poly-3-hexyl-thiophene/poly-methyl-methacrylate (P3HT/PMMA) blends to improve the performance of water-gated organic field-effect transistors" by Loïg Kergoat and coworkers.

The paper reports on organic transistors in which the active layer is made of a blend of semiconductor and insulating polymers., and the gate dielectric consists of the electrical double layer that forms at the interface between the semiconductor blend and a drop of pure water. It is found that, besides the very low operating voltage brought by the electroyte-gated structure, the use of a blend also improves the on/off current ratio. An optimum value of the proportion of the insulating polymer in the blend is found at 70%.

Gilles Horowitz
Paris, July 21, 2010

***Detailed Response to Reviewers**

"Use of poly-3-hexyl-thiophene/poly-methyl-methacrylate (P3HT/PMMA) blends to improve the performance of water-gated organic field-effect transistors"
by Loig Kergoat, Nicolas Battaglini, Luciano Miozzo, Benoit Piro, Minh-Chau Pham, Abderrahim Yassar, Gilles Horowitz

Reply to the referee

We would like to thank the referee for additional comments. The changes done in the revised version are highlighted in yellow, and detailed hereafter.

1. Reference is made to a recent work by MC Wu and coworkers that indeed observe our conjectured partial dilution of P3HT into PMMA (page 5 and new reference 26)
2. The explanation put forward by the referee has been added, together with the suggested reference (page 6 and references 30 and 31)
3. We agree with the referee. Mentions to increased stability have been withdrawn.
4. Corrections have been made.

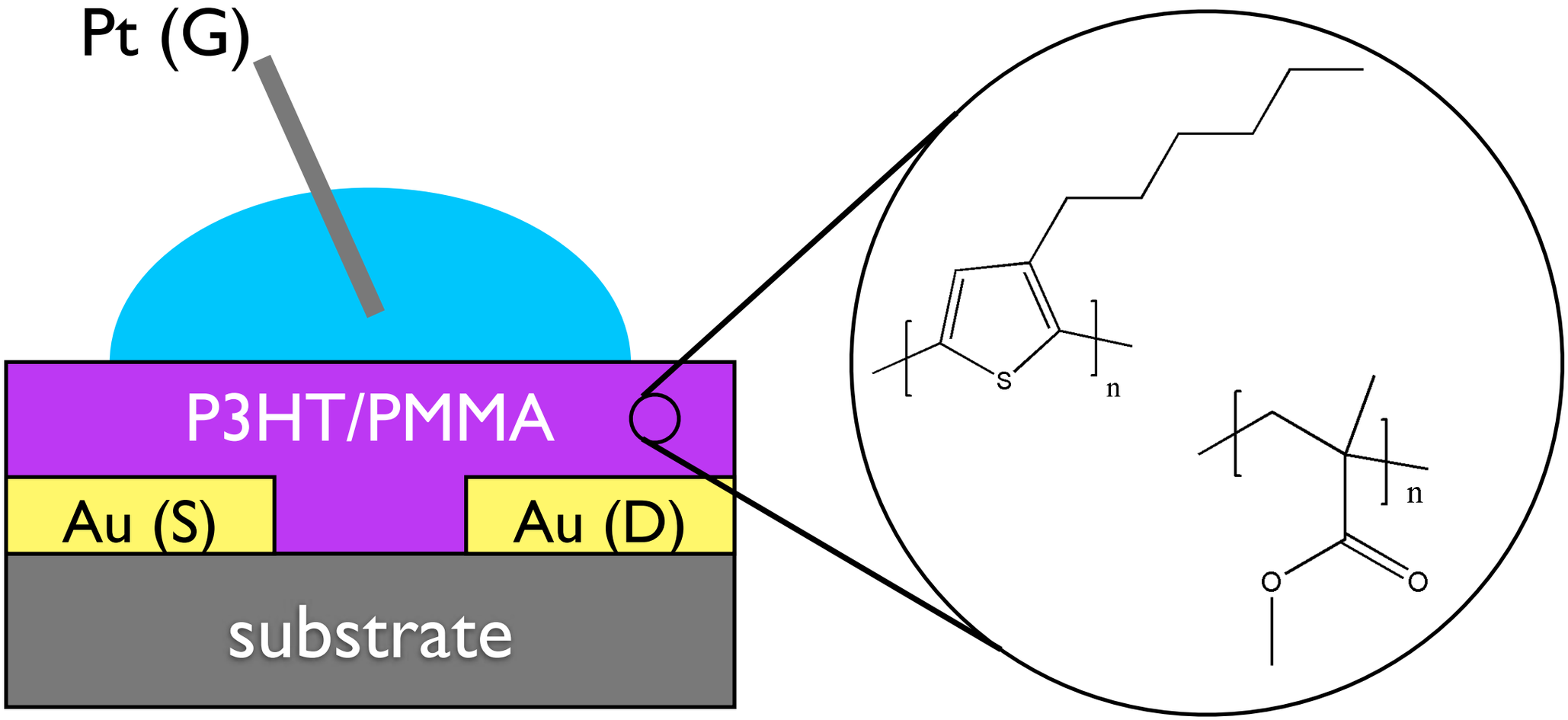
***Research Highlights**

“Use of poly-3-hexyl-thiophene/poly-methyl-methacrylate (P3HT/PMMA) blends to improve the performance of water-gated organic field-effect transistors”
by Loig Kergoat, Nicolas Battaglini, Luciano Miozzo, Benoit Piro, Minh-Chau Pham, Abderrahim Yassar, Gilles Horowitz

Research highlight

- Water-gated organic field-effect transistors operate in the field-effect mode at very low voltages.
- Blends of the semiconductor P3HT and insulating PMMA polymers have mobility similar to that of pure P3HT with concentration of PMMA up to 70%.
- Drain current on/off ratio reaches an optimum value for a PMMA concentration of 70%.

*Graphical Abstract



Use of poly(3-hexylthiophene)/poly(methyl methacrylate) (P3HT/PMMA) blends to improve the performance of water-gated organic field-effect transistors.

*Loig Kergoat, Nicolas Battaglini, Luciano Miozzo, Benoit Piro, Minh-Chau Pham, Abderrahim Yassar, Gilles Horowitz**
ITODYS, Univ Paris Diderot, 15 rue Jean Antoine de Baïf, 75205 Paris cedex 13, France

Abstract

Poly(3-hexylthiophene)/poly(methyl methacrylate) (P3HT/PMMA) blends were used as the semiconducting layer in water-gated organic field-effect transistors (OFETs), which resulted in improving the electrical performance of the previously reported devices with pure P3HT. Topographic investigations by atomic force microscopy carried out on blends with various PMMA to P3HT ratio reveal a lateral phase separation of the two components. All transistors operate at very low voltage (below 1 V), with a threshold voltage ranging form 0.3 to 0.5 V. An optimum of the composition of the blend is found with 70% of PMMA, leading to a maximum on/off current ratio and a mobility comparable to that of pure P3HT.

Introduction

For the past twenty years, organic electronics has known a growing interest. Its low fabrication cost combines with a large scale manufacturing and integration to electrical circuits on flexible substrate capability. Although the performance of organic semiconductors will probably reamain lower than that of crystalline silicon-based electronic devices, it is continuously improving. Highly ordered organic solids such as rubrene single crystals and polycrystalline pentacene can achieve a charge carrier mobility up to 20 $cm^2/V\ s$ [1] and 5 $cm^2/V\ s$, [2] respectively, while charge carrier mobility is limited to 1 $cm^2/V\ s$ in amorphous silicon. However, these compounds do not fit low cost processes and chemical modifications are needed to achieve this goal.[3]

On the other hand, disordered polymeric semiconductors are easily processable, but suffer from low mobility (below 0.1 $cm^2/V\,s$). Alongside with the synthesis of new materials, recent progress have been made at improving the quality of known materials. A widespread method for this approach is to blend several materials with the desired properties. It has been used for long in the case of non-conjugated polymers to improve their mechanical properties. For the past 15 years, the technique has been extended to conjugated polymers, especially in optoelectronic devices such as organic light emitting diodes[4,5] and photovoltaic cells.[6] OFETs made of blends are less common. However, a few examples have been recently reported using inorganic nanoparticles[7,8] especially with semiconductor/semiconductor[9,10,11] or semiconductor/insulator blends[12]. These works have shown that blending materials could improve both air stability[13] and mobility of charge carriers.[14,15] A one-step procedure for the formation of the gate dielectric and semiconductor is even possible by taking advantage of the self-organisation of the two components.

Another concern for low-cost organic electronics is to lower the operating voltage of OFETs. This can be achieved by increasing the capacitance of the gate dielectric. The strategies that have been developed to achieve low-voltage operation include cross-linked polymers,[16] self-assembled monolayers[17,18] and the use of electrolytes.[19,20] The latter can achieve very low voltage ranges due to the very high electric field generated at the interface between the electrolyte and the organic semiconductor. Mobile ions inside the electrolyte move to form an electric double layer (EDL) at the interface, with a capacitance that can reach several hundreds of $\mu F/cm^2$ [19, 21, 22]. These devices typically operate below 1 V. Furthermore, increasing the capacitance leads to an increase of the charge carrier mobility for polymer semiconductors and the subsequent increase in the output current.[23]

In a previous work,[24] we successfully used pure water to isolate the gate from the semiconductor. We managed to show that within the water stability potential range, our devices run in the field-effect mode with negligible electrochemical reactions, which is usually the main issue for electrolyte-gated OFETs.[25]

Here, we investigate the use of semiconductor/insulator blends as active layer in water-gated OFETs in order to improve the performance of the device.

Experimental

Materials

Poly(3-hexylthiophene) (P3HT) (MW=37 000 g.mol^{-1}, 98% regioregular) and poly(methyl methacrylate) (PMMA MW=120 000 g.mol^{-1}) were purchased to Sigma-Aldrich and used without further purification. Chlorobenzene was purified by distillation.

Solutions of P3HT/PMMA (1% wt) blends with different ratios were prepared as followed. First PMMA was dissolved in chlorobenzene by stirring overnight. Then P3HT was added to the PMMA solution and stirred until the P3HT is totally dissolved. Finally, solutions were filtered with a 200 nm polytetrafluoroethylene (PTFE) filter.

OFETs preparation

A general view of the device is sketched in Figure 1 together with the chemical structure of P3HT and PMMA. The transistors were built in a bottom contacts and top gate configuration. The substrate consisted of a silicon wafer with 300 nm thermally grown oxide. Contacts were made of evaporated gold patterned by conventional micro-lithography. P3HT/PMMA solutions were spin-coated onto the substrates at 1500 rpm for 30 s in ambient conditions. The devices were then kept overnight in an oven at 110 °C under a pressure of 50 mbar to remove the residual solvent.

A water droplet was generated with a calibrated micro-syringe and deposited onto the semiconductor. The water used was obtained from a Elgastat UHQ II purification system with a resistivity of 18 MΩ.cm. In ambient conditions, the main contaminant of water is dissolved carbon dioxide, which forms carbonic acid that dissociates in turn into hydrogenocarbonate and hydronium ions with a concentration of about 10-6 mol/L. The concentrations of other species in solution are negligible. The gate electrode consisted of a platinum wire dipped into the droplet.

Electrical characterization and thin-films morphological study

Electrical measurements were realised using a semiconductor parameter analyzer (Keithley 4200-SCS) in a humid environment to prevent the water droplet from drying. Before measuring each blend, the platinum wire was cleaned in an ultrasonic bath for 10 min in deionized water and 10

min in acetone then put in a UV surface decontamination system (Novascan PSD-UV) for 15 min to get rid of any trace of organic contamination.

Three different channel lengths (3 µm, 10 µm and 40 µm) were used and for each length, six transistors were tested. The reported data correspond to the mean of these six measurements. Atomic force microscopy was realised on a multimode SPM with Nanoscope III controller (Digital Instruments) in tapping mode on thin-films deposited on silicon wafers with thermally grown oxide (300 nm).

Results and discussion

Figure 2 shows AFM 10x10 μm^2 topographic images of the P3HT/PMMA films with various weight ratios. Blends with PMMA concentrations up to 30% (Figures 2 a and b) do not show any clear phase separation at this scale. However, an abrupt decrease of the RMS roughness (Figure 2 f) occurs, indicating an enhancement of the homogeneity due to the increase of PMMA content (RMS roughness of pure PMMA was found to be below 0.5 nm). For a ratio of P3HT/PMMA of 1:1 (Figure 2 c), lateral phase separation clearly occurs as indicated by the dark nanospheres of PMMA into a matrix of P3HT. With 70% of PMMA (Figure 2 d), the two phases tend to form two continuous networks that extend all over the film, as indicated by the 30x30 μm^2 image given in the inset. Increasing the PMMA weight ratio to 90% (Figure 2 e) results in isolated nanospheres of P3HT. Furthermore, above this amount of PMMA, the roughness decreases to reach a plateau that extends up to 70% of PMMA, resulting in a smoother film. A further decrease of the roughness occurs for PMMA concentrations above 70%. This trend is also observed when measuring the roughness of the domains composed of P3HT only. We note that a similar behavior has been recently reported on P3HT/PMMA blends.[26]

All OFETs made of polymer blends show a typical p-channel behavior. Output characteristics of pure-P3HT and blend with 70% of PMMA are presented in Figure 3.

The field-effect mobility of holes was extracted from the transfer characteristics in the saturation regime (Figure 3 c). The mobility is estimated from the slope of the $I_d^{1/2}$ vs. V_g curve and the capacitance used is that measured in a previous work;[24] data for various blend ratios are gathered in Figure 4 a. Three different channel lengths have been used. Increasing the channel length from

3 µm to 40 µm improves the effective mobility by almost one order of magnitude. This phenomenon is well documented and is a consequence of contact resistance.[27, 28] For small channels, the contact resistance considerably reduces the effective mobility. This lowering is less pronounced as the channel length increases.

For pure-P3HT spin-coated from a chlorobenzene solution, the highest mobility with a 3 µm channel length is 0.03 cm^2/V s, which is higher than what reported in our previous work where the film was deposited from a chloroform solution.[24] We attribute this increase to the highest boiling point of chlorobenzene. Chloroform is widely used as solvent for P3HT. However, due to its low boiling point (62°C) and fast evaporation rate, the corresponding films have a lesser degree of crystallinity. It has been shown that the use of a higher boiling point solvent such as chlorobenzene (132°C) leads to an improvement of the mobility due to a higher crystallinity consecutive to a slower evaporation speed.[29]

Of interest is that in blends, the mobility remains practically constant within a broad range of PMMA concentration (up to 70%). As the phase separation is lateral, one would expect a variation of the mobility due to a decrease of the P3HT area at the interface. Instead, it seems that the percolation paths observed on the AFM pictures suffices to warrant a good charge carrier transport through the blend. However, above 70% of PMMA, P3HT domains change into isolated islands, leading to discontinuous conducting paths and a subsequent lowering of the hole mobility.

Blends with 90% of PMMA show a clear (although substantially reduced) field-effect behavior. The presence of a thin P3HT film on top of the blend (vertical phase separation) is unlikely because it is at variance with the observed decrease of the RMS roughness. Instead, we attribute this reduced charge transport capability to a partial dilution of P3HT into the PMMA matrix; although this hypothesis would deserve further investigations, evidence for it can already be found in the literature.[26]

Figure 3 c shows the transfer curves, in the saturation regime, for pure-P3HT and P3HT:PMMA 3:7 blend. The on current is almost identical in both cases, while the off current is lowered by one order of magnitude for the blend, thus resulting in a significant increase of the on/off ratio. The dependence of the on/off ratio with the composition of the blend is shown in Figure 4 b; it increases

up to 5000 when decreasing the P3HT concentration down to 30%. Below this value, the on/off ratio drops down to the value of pure-P3HT, because of the drop of the on current, while the off current still decreases. Several explanations can be put forward. One is the fact that the formation of insulating domains decreases the leakage current. An alternative explanation would be the decrease of the charge density at the semiconductor/water interface resulting of the lowering of the P3HT concentration in the film, because the off current is known to be inversely proportional to the charge density.[30,31] Of interest is the fact that for high PMMA concentrations (above 50%), the off current measured on the transfer curves does not depend on the drain voltage (Figure 3 c). Finally, Figure 4 c shows the variation of the threshold voltage as a function of the concentration of PMMA. A threshold voltage close to 0 V is desired for low-voltage applications. In the blends, this voltage shifts towards more positive values for PMMA concentration above 50%, yet remaining at a low level (< 1 V).

Conclusion

Used in a water-gated configuration, P3HT/PMMA blends can lead to transistors with reasonably high mobility (up to 0.15 $cm^2/V.s$) working at very low voltage (below 1 V). The mobility is not affected when increasing the proportion of PMMA up to 70%, while the off current is significantly lowered, thus resulting in an enhancement in the on/off ratio. AFM images showed that up to 70% of PMMA, a percolation path exists, thus allowing an efficient charge transport through the channel, in good agreement with the electrical measurements

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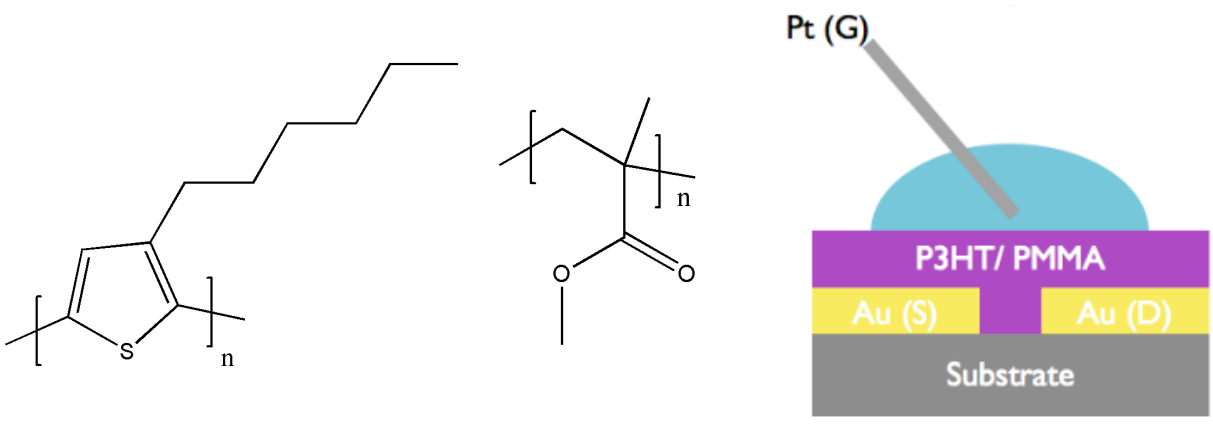


a) b) c)

Figure 1. Chemical structure of a) P3HT and b) PMMA. c) Cross-section of the water-gated OFET.

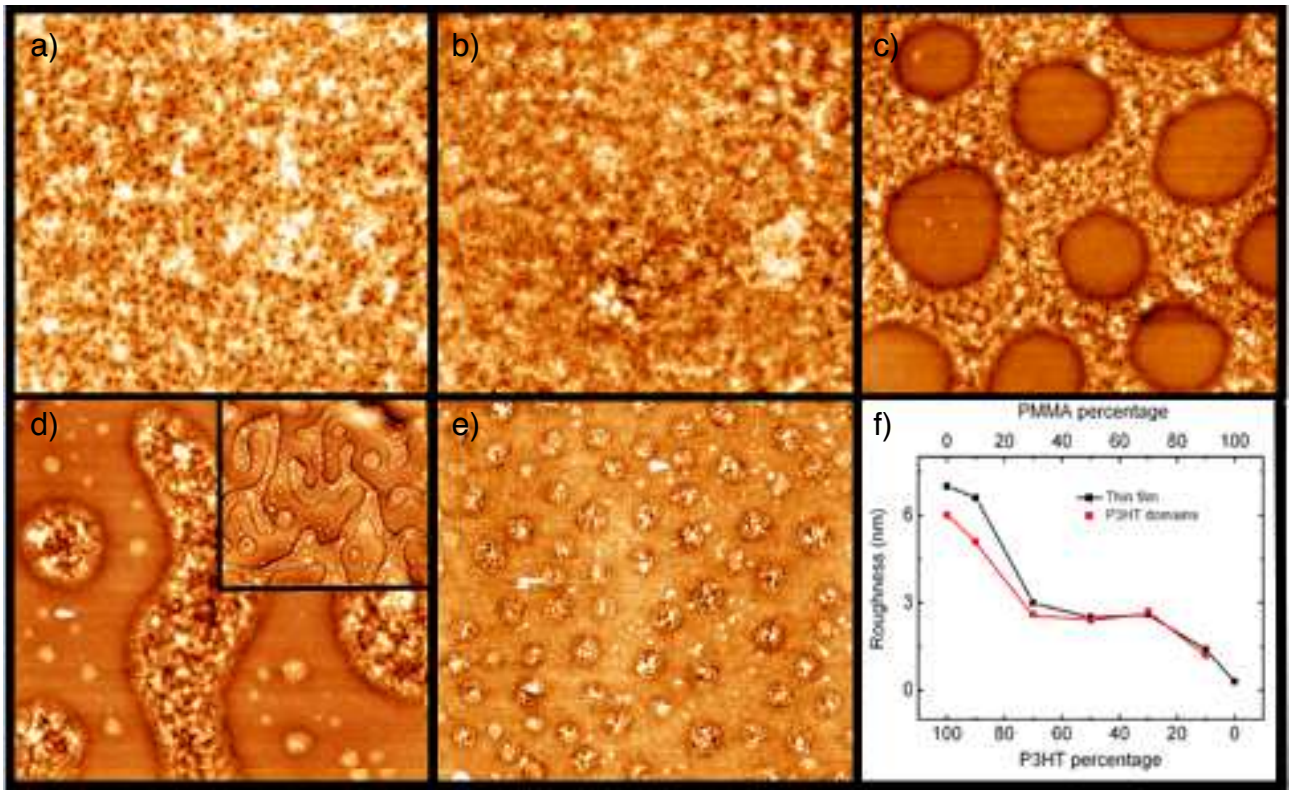


Figure 2. AFM topographic images (10x10 μm^2) of a) 100%, b) 70%, c) 50%, d) 30% (the inset shows the topography of a 30x30 μm^2 image) and e) 10% of P3HT/PMMA blend thin films. f) RMS roughness as a function of P3HT percentage. The RMS was estimated over the whole image or over the P3HT domains only.

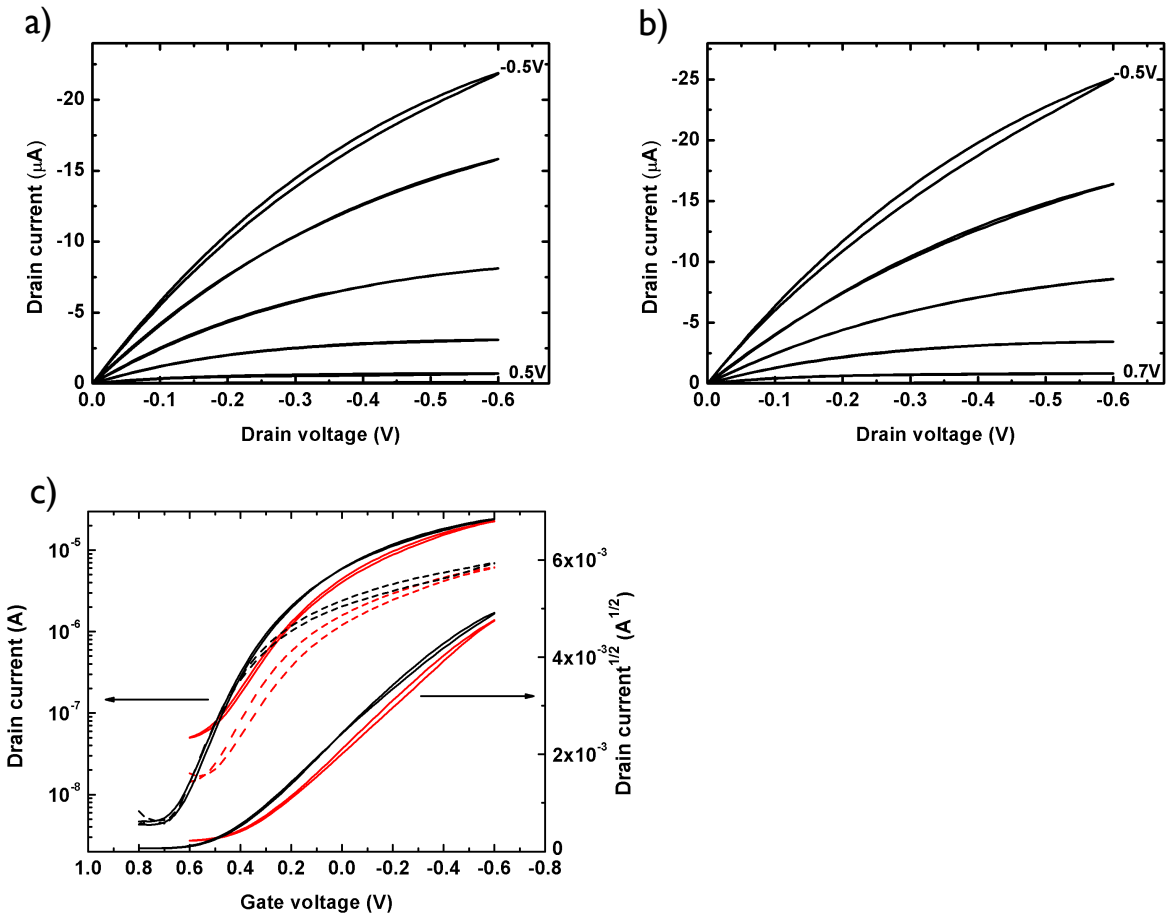
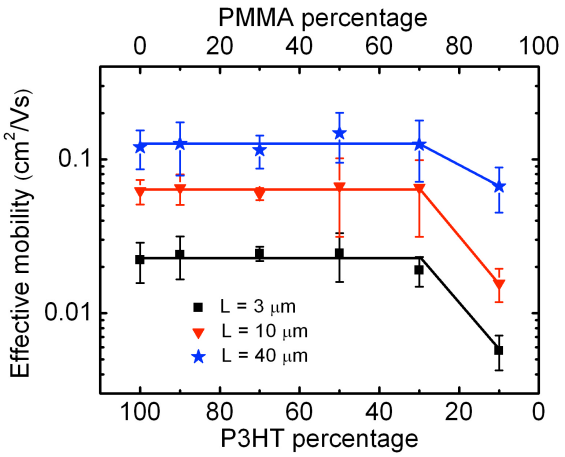


Figure 3. Output curves of OFETs with a) pure P3HT and b) P3HT:PMMA 3:7 blend. c) Transfer curves of homo-P3HT (red line) and P3HT:PMMA 3:7 blend (black line) plotted in a semi-log scale (left scale) for V_d=-0.1 V (dashed line) and V_d=-0.5 V (full line) and in a square root scale (right scale) for V_d=-0.5 V.

a)



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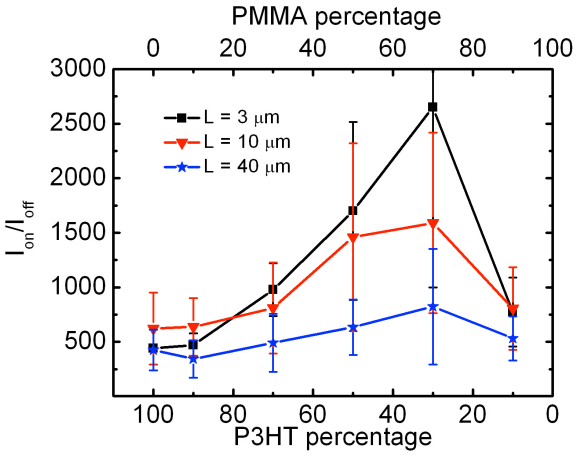

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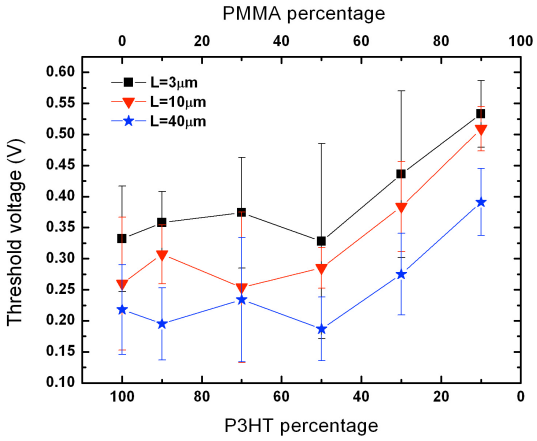

Figure 4. Compositional dependence of the a) effective hole mobility; b) I_{on}/I_{off} ratio and c) threshold voltage. The data and error bars are estimated from the measurements on six different devices.